Overview of DOD Perchlorate Efforts

Bryan Harre
Naval Facilities Engineering Service Center
1100 23rd Avenue, Code 411
Port Hueneme, CA 93043
Phone: 805-982-1795 E-mail: harrebl@nfesc.navy.mil

Perchlorate originates as a chemical found in the environment from the solid salts of ammonium, potassium, or sodium perchlorate. The perchlorate anion is quite soluble in water. The resultant anion ($C10_4$-) is very mobile in aqueous systems. It can persist for many decades under typical groundwater and surface water conditions because of its resistance to react with other available constituents.

Ammonium perchlorate is manufactured for use as the oxidizer component and primary ingredient in solid propellant for rockets, missiles, fireworks, and some munitions. Large-scale production began in the United States in the mid-1940s. Because of its shelf life, it must be periodically washed out of the country's missile and rocket inventory and replaced with a fresh supply. Thus, large volumes of the compound have been disposed of since the 1940s.

Perchlorate is of concern because of: 1) Potential health effects at low concentrations; 2) the possibility that perchlorate may be widespread in the environment; 3) the expense of removing perchlorate from water and soil; and 4) the effects that perchlorate may have on ecosystems.

There is currently no federal National Primary Drinking Water Regulation for perchlorate. It is on the EPA's Safe Drinking Water Act Contaminant Candidate List, but before a determination to regulate can be made, data gaps must be filled regarding occurrence, health effects, treatment technologies, and analytical methods. Finding these answers for perchlorate is a very high priority. The data generated by the Unregulated Contaminant Monitoring Rule (UCMR), which includes all of the compounds on the contaminant candidate list, will be used to evaluate and prioritize contaminants on the Drinking Water Contaminant Candidate List.

The EPA established a provisional reference dose (RfD) range based on assessments of existing information in 1992 and revised in 1995. By applying the standard default body weight (70 kg) and water consumption level (2 L/day), the resulting provisional cleanup or action levels would range from 4-18 parts per billion (ppb). This level currently represents agency policy, which was reaffirmed in January, 2003.

The current EPA draft human health risk assessment has a revised oral human health risk benchmark of 0.00003mg/kg-day. By applying the standard default body weight (70 kg) and water consumption (2 L/day) values, a drinking water equivalent level (DWEL) would be calculated at 1 ppb. It is important to note that this assessment is in draft form and does not represent agency policy. Following the establishment of a final harmonized oral human health risk benchmark for perchlorate, the EPA will develop a drinking water Health Advisory.

Certain states have begun the process of regulating perchlorate. In 1997, California established a provisional action level of 18 ppb for perchlorate in public water supplies. In January 1999, CA DHS adopted a regulation identifying perchlorate as an unregulated chemical for which monitoring is required. Certain drinking water systems are required to sample their drinking water sources for perchlorate. The reported perchlorate detections in public water systems and drinking water sources, as of June 3, 2002 in CA are 11% of public water systems and 6.6% of drinking water sources. This number is twice the impact that MTBE has had to date in the state.

In January, 2002 CA changed its provisional action level for perchlorate to 4ppb. This change was prompted by EPA's January, 2002 release of the "Perchlorate Environmental Contamination: Toxicology Review and Risk Characterization" This level is still however based upon the 1995 peer reviewed data, which allowed for a level between 4 and 18ppb.An action level is an unenforceable notification level that requires drinking water systems exceeding this level in potable water to notify their local governing body. . The CA DHS then recommends notifying the public of this fact. Some drinking water purveyors in the state have stopped serving water over the action level for fear of potential litigation. Surface water (Colorado River) does not have the reporting requirements or recommendations.

In March, 2002 the California EPA Office of Environmental Health Hazard Assessment (OEHHA) Draft Public Health Goal(PHG) for Perchlorate was released for public comment. The PHG document relies heavily upon the latest EPA assessment for perchlorate for the science to generate the numbers for the PHG. Some of the key differences are that the PHG is based upon the use of human data to generate the PHG, the use of a relative source contribution factor (0.6), and a lower uncertainty factor of 30. Their latest assessment from December, 2002 results in a PHG range from 2-6 ppb.

The schedule for the establishment of a PHG in CA includes a number of events. OEHHA's establishment of a PHG required a public meeting (April 29). The purpose of the meeting was to allow the public to comment on the PHG. Following the meeting, OEHHA will revise the document as appropriate, and make it available for a 30-day public review and scientific comment period. This second review and comment period was announced in December 2002 and published in the California Regulatory Notice Register and posted on the OEHHA Web site. The responses to the major comments from the public at the workshop and during the two public review and scientific comment periods, as well as from peer reviewers at the University of California system and state and federal agencies, will also be available on the OEHHA Web site. A final PHG is expected in 2003. An MCL is expected in 2004.

In October, 2001 Texas revised its interim action level for perchlorate in drinking water from 22 ppb to 4 ppb. The Texas Risk Reduction Program (TRRP) residential groundwater cleanup standard is also 4 ug/L. The TRRP commercial/industrial groundwater cleanup standard is now 7 ug/L. The Risk Reduction Rule (RRR) residential groundwater cleanup standard is 4 ug/L. The RRR commercial/industrial groundwater cleanup standard is 10 ug/L.

Since perchlorate was discovered in water supplies in California, Nevada, and Arizona, much progress has been made in developing treatment methods capable of removing perchlorate from water. Over 65 perchlorate treatment technology projects have been funded. Agencies funding this research include the American Waterworks Association Research Foundation, DOD's Strategic Environmental Research and Development Program (SERDP), DOD's Environmental Security Technology Certification Program (ESTCP), the National Science Foundation, several universities, water utilities, and Department of Defense activities. Most of the attention has been directed at two technologies: biological treatment and ion exchange.

In the biological treatment process, microbes destroy perchlorate by converting the perchlorate ion to oxygen and chloride. In most cases, nutrients must be added to sustain the microbes. A full-scale system at a Superfund Site in Northern California, where perchlorate concentrations exceed 1,000 ppb, has been operating for a number of years. A biological process has also been used to treat perchlorate-containing wastewaters resulting from the manufacture and maintenance of rocket motors, where perchlorate concentrations may exceed 500,000 ppb. In-situ bioremediation has also been pilot tested at the Aerojet site, with promising results. Aerojet has also demonstrated a biobarrier approach at its site with help from SERDP. Results have reduced the perchlorate concentration to the reporting limit of 4ppb. Barrier walls using biological treatment have been implemented at full-scale at the Naval Weapons Industrial Reserve Plant in McGregor, Texas. This site has also implemented the injection of carbon sources to form a biobarrier. ESTCP has funded and will be performing three demonstrations of in-situ bioremediation over the next two years.

A biological treatment method is capable of producing potable water, and has just recently been approved for drinking water applications. Biological treatment methods are new to drinking water utilities, but biologically-active filters have been used in drinking water treatment for decades to help remove particles and biodegradable organic matter. The approved treatment train relies upon biological treatment for primary removal of perchlorate, and includes an intensive sampling program to determine process parameters.

The second of the two perchlorate-removal technologies receiving the most attention is ion exchange. In ion exchange the perchlorate ion is replaced by chloride, a chemically similar but nontoxic ion. Ion exchange processes have been used in homes and businesses for water softening for decades. Bench, pilot, and full-scale studies have demonstrated that ion exchange systems can reliably reduce perchlorate concentrations and are approved for drinking water use in California.

The principal disadvantage of ion exchange systems is that they produce a concentrated brine that requires disposal and/or further treatment. Research is underway to try to identify methods of reducing the volume of perchlorate-contaminated brines to reduce the high cost of disposal. A catalytic destruction unit to destroy the brine has been developed. This unit has been installed at full-scale at the Henderson, Nevada site and is approved for drinking water applications in California.

Currently, ion chromatography (IC) is the analytical method for the measurement of perchlorate in water. Federal, state, and private laboratories collaborated to study the existing IC method and its variations. The study design evaluated the within laboratory precision (repeatability), between laboratory precision (reproducibility), method accuracy (bias), detection limit, and sensitivity of the method. The net result of this testing is EPA method 314 *Determination of Perchlorate in Drinking Water Using Ion Chromatography*, which has a reporting limit of 4 ppb for perchlorate.